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(54) Process and Apparatus for Fractionation of a Gaseous Mixture

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PROCESS AND APPARATUS FOR FRACTIONATION
OF A GASEOUS MIXTURE

Background of the Invention

5 This invention relates to a system for the fractionation of a gaseous mixture, especially hydrocarbon mixtures, by distillation, especially at low temperatures wherein either components of the gaseous mixture form a substantially azeotropic mixture or at least one of the components of the gaseous mixture tends to freeze out.

10 By way of definition, the term "distillation" used herein is intended to embrace rectification as well as other conventional distillation processes. The term "substantially azeotropic mixture" is intended to embrace true azeotropic as well as approximate (pseudo) azeotropic mixtures e.g., equilibrium mixtures of CO₂ with H₂S which at certain constant pressures exhibit CO₂ concentrations in the vapor phase that are everywhere greater than those in the liquid phase, but where the concentrations of CO₂ in the vapor and liquid phases are nearly identical over an extended composition range.

20 Fractionation processes pertinent to this invention have been described in "Hydrocarbon Processing", May 1982, pp. 131-136. If a gaseous mixture is to be fractionated wherein the components during distillation form a substantially azeotropic mixture, then product purity is limited by the concentration of the components at the azeotropic point. In the distillation of other gaseous mixtures at low temperatures, where the reflux liquid is insufficient to maintain all of the components in solution at the cold temperatures, one or more of these components begin



to freeze out, thereby terminating the distillation.

One suggested solution to the problem proposed in the aforementioned prior publication resides in admixing to the reflux liquid in the column an additional component, 5 such as n-butane or a mixture of light or heavy hydrocarbons. Such admixture has the effects of increasing the amount of reflux liquid, altering the composition of the liquid, and increasing the temperature in the column. These effects, in the one case, suppress the deposition of 10 solids which would otherwise freeze out, and in the other case with azeotropic mixtures results in an improvement of the purity of the fractionation products. The added components are then withdrawn from the distillation column and recovered in a supplemental distillation 15 stage.

This suggested process, however, has several disadvantages. For example, in the separation of the additional component in the downstream supplemental distillation stage another azeotropic mixture occurs in part, for example ethane 20 and carbon dioxide. Consequently, an additional component must also be introduced into this supplemental downstream distillation stage and this increases the cost of the process.

A further disadvantage resides in that the additionally 25 introduced component causes dilution of the reflux liquid in the column, thus increasing the work of separation in the column. Still another disadvantage is that the additional component that must be fed to the column 30 as a cold liquid is heated, during its downward flow within the column, to the higher temperature of the liquid in the column sump, so that a large portion of the cold value is dissipated.

Summary

An object of one aspect of this invention is to provide one or more processes of the type mentioned hereinabove but which exhibit improved economics for 5 the separation of gaseous mixtures containing components tending to freeze out or form substantially azeotropic mixtures.

According to an object of another aspect of this invention, apparatus is provided for conducting such 10 improved processes.

Though the process of this invention is applicable to gaseous mixtures containing substantially azeotropic mixtures or components which tend to freeze out, it is to be understood that the two types of gaseous mixtures 15 exhibit different problems, and that in the absence of this invention, there would be no suggestion that the invention disclosed herein could be used for both types of mixtures.

According to the first aspect of this invention, a 20 system is provided wherein during distillation, at least a partial stream containing components of the substantially azeotropic mixture, and/or of the component(s) tending to freeze out is removed from the column, subjected to separating to deplete the removed distillation medium in components of 25 said substantially azeotropic mixture or component(s) tending to freeze out, and resultant depleted distillation medium is recycled to the distillation column.

In the process of this invention, a vapor-phase or liquid fluid is withdrawn from the fractionating 30 column, preferably as a side stream, e.g., from a plate above the bottom plate and below the top plate, the composition of the fluid is changed, and then the resultant altered fluid returned into the column in the vapor or

liquid phase. In direct contrast to the previously known process, altering of the composition takes place by separating specific components from the fluid to be returned to the column, rather than by adding an additional component.

- 5 It is possible by the process of this invention to fractionate gaseous mixtures tending to form azeotropic mixtures or tending to produce solid deposits in the fractionating column. This eliminates the difficulties inherent in the prior art method of introducing an additional component. Distillation
- 10 in this invention is thus improved by separating part of the gaseous components.

In particular, when a component which tends to freeze out is removed, not only is there an advantage because of a reduction in the concentration of this component in the column, resulting from the increased reflux liquid from the recycled stream, but there is also an advantage because the effective amount of this component is reduced, which reduces the work required for separating this component in the column. This compensates for the work required to separate the component in the supplementary separation process.

In an advantageous further aspect of the process of this invention, the fluid to be returned is withdrawn approximately at the level of the middle or upper third of the column, e.g., in a column of 20 theoretical plates, the fluid is withdrawn at anywhere from the 2nd to the 19th plate.

In the case of approximate azeotropic mixtures, the fluid may be withdrawn anywhere from the 2nd to the 19th plate, whereas in the case of freezing of components it is withdrawn from about the 10th to the 19th plates.

- 30 The recycle of the fluid admittedly entails a certain.

dilution of the process streams in the column, but this dilution is restricted to a limited zone of the column, whereas in the conventional introduction of an additional component, the entire column, down to the sump, is traversed by a stream of dilute reflux liquid. The cold values contained in the withdrawn fluid can be utilized for cooling the gaseous mixture

to be fractionated or, in conjunction with a heat pump, for cooling the head of the column. Therefore, the process as conducted according to this invention not only prevents freezing out, but also improves the economics 5 of the distillation step.

In a preferred embodiment of another aspect of the process of this invention, separation of the withdrawn distillation medium is conducted by a physical or chemical scrubbing step.

10 In another advantageous aspect of the process of this invention, the separation is conducted by diffusion on semipermeable membranes.

Because of their substantially different diffusion characteristics, acid gases, e.g., H_2S or CO_2 , can 15 be separated by diffusional processes from methane, ethane and/or higher paraffins. The use of semipermeable membranes for this purpose is highly economical with respect to both apparatus costs and energy consumption. Such semipermeable membranes are conventional and include, 20 but are not limited to:

cellulose acetate, polysulfanone, silicone rubbers, polyesters.

Cellulose acetate is preferred for the separation of CO_2 and C_2H_6 , but the choice of membrane will depend on the 25 actual components to be separated, and the operating conditions of the membrane, and other equipment.

For further details on the separation of gases by membrane permeation, reference is made, for example, to Perry and Chilton, Chemical Engineer's Handbook, 30 5th Edition, 1973, McGraw-Hill, pp. 17-34 through 17-38.

In a preferred further aspect of the process of this invention, the gaseous mixture to be fractionated contains an acid gas and a hydrocarbon. Suitable acid gases include, but are not limited to, CO_2 and H_2S ;

suitable gaseous hydrocarbons include, but are not limited to, methane, ethane, and propane. Examples of gaseous mixtures to be fractionated in percent by volume are:

5 (A) CH_4 (about 5 to 20 %), CO_2 (about 50 to 90 %) and C_2H_6 (about 2 to 10 %); and (B) C_4H_{10} (about 10 to 50 %), C_3H_8 (about 10 to 50 %), H_2S (about 10 to 50 %) and C_2H_6 (about 10 to 50 %). *

Advantageously, the gaseous mixture contains an acid gas as well as two other components having different 10 boiling points, and in particular, the distillation medium to be recycled is withdrawn from the column at the zone of the highest concentration of the component having the intermediate boiling point.

If the mixture contains, for example, an acid gas, 15 as well as methane and ethane as the other components, then the medium to be recirculated is withdrawn from the column at the zone of the highest ethane concentration in the latter. Since ethane is capable of dissolving large amounts of acid gas, and moreover increases the 20 temperatures at the column plates, this aspect of the invention is of special advantage for the fractionation. Although a maximum in ethane concentration would occur in the column even without the separation of the component tending to freeze out, the separation step 25 of this invention substantially enhances this effect. Thus, it would be necessary to determine the location in a column of the maximum ethane concentration and at substantially that location, withdraw the side stream from the distillation medium.

30 The formation of a high ethane concentration is especially beneficial if, in a further aspect of the process of this invention, the depleted distillation medium is returned into the column above the point of withdrawal.

* (A) is a mixture containing components which tend to freeze out,
(B) is a mixture containing substantially azeotropic mixtures.

A high ethane concentration not only prevents freezing out of acid gas, but also additionally increases the amount of reflux in the column and moreover increases the efficiency of the diffusion process -- if semipermeable membranes are used for separation purposes. The reason for this increased efficiency is that the relative permeability of, for example, cellulose acetate membranes for, e.g., CO_2/CH_4 -mixtures is about ten times as low as for $\text{CO}_2/\text{C}_2\text{H}_6$ -mixtures. As a consequence, the acid gas can be separated from the withdrawn distillation medium without a large loss of ethane. By using the operating procedure of the process described with reference to the hereinafter described example of separating an acid gas-methane-ethane mixture, the largest part of the methane can also be recovered.

Since ethane has a higher concentration in the liquid than in the vapor phase, the distillation medium to be recycled is suitably withdrawn from the column in the liquid phase. Inasmuch as liquid ethane is a good solvent for the acid gas component tending to freeze out, the acid-gas-depleted distillation medium is also suitably returned into the column in the liquid phase.

In the fractionation of gaseous mixtures tending to form azeotropic mixtures, it may be advantageous under certain circumstances to return the fluid to be recycled at below the point of withdrawal into the column. The exact positions where the fluid should be removed and returned to the column depend upon the composition profiles in the column and upon the influence of composition changes on the phase equilibria of the fluids within the column, and upon the specifications for the products of the column and supplementary separating process. The recycling of the depleted stream to a point below the point of removal would normally be required in the case of an approximate azeotropic mixture occurring in the lower part of the column,

said mixturing being such that an improvement in separation may be achieved by addition of a component present in the upper part of the column.

Recycling of the depleted stream to a position above
5 the point of removal would normally be required in the case of either the freezing of one or more components or in the case of an approximate azeotropic mixture occurring in the upper part of the column, said mixture being such that an improvement in separation may be obtained by
10 addition of a component present in the lower part of the column.

In an advantageous further aspect of the process of this invention, the acid gas component of the distillation medium recycled into the column is at most 5 and preferably no more than 3 mol% of the recycled medium. The acid gas 5 proportion may, in any case, only be of such a magnitude that no solids are precipitated during recycling into the column.

If the fluid withdrawn from the column is conducted over semipermeable membranes, it must be compressed beforehand so as to at least compensate for the resultant pressure 10 loss. Compression also simultaneously contributes to part of the refrigeration required in the process. As a result of the increased pressure ratio the separation of the components can be made sharper. A high ethane concentration also contributes to a sharp separation because the rate of 15 permeation of ethane is very low compared to the acid gases, e.g., CO₂. Alternatively, for a constant pressure ratio, the pressure on the low pressure side of the membrane may be increased. A superatmospheric pressure is desirable to prevent ingress of air which could produce explosive mixtures with 20 any hydrocarbons contained in the permeate stream; it also obviates the need for an expensive and energy intensive vacuum compressor.

In a further embodiment of the process of this invention, the gaseous stream diffusing through the semipermeable 25 membranes, which stream contains essentially acid gas, e.g. CO₂, is mixed with the sump product of the column also rich in CO₂. These CO₂ streams are reused, for example, in tertiary oil recovery. Details of a tertiary oil recovery process employing CO₂ or the like are found in the literature, e.g.,

B.C. Price, F.L. Gregg "CO₂/EOR: from source to resource"
62nd Annual GPA Convention March 14-16 1983, San Francisco,
published also in Oil & Gas Journal, Aug. 22, 1983.

In a preferred further development of the process of this invention, the gaseous mixture to be fractionated comprises natural gas or a gaseous petroleum component, e.g., propane. This invention is especially applicable to the distillation 5 of a gaseous mixture which is a gas recovered from a tertiary oil recovery process, wherein CO₂ is injected as the motive gas into a well

hole for expelling and reducing the viscosity of oil as discussed above. Thus, (a) the feed gas into the well hole and (b) the withdrawn gas from the formation respectively comprises: (a) the separated CO_2 fraction and (b) the feed gas associated with the distillation process of this invention.

Brief Description of Drawings

FIGURES 1, 2 and 5 are schematic flowsheets showing three different preferred embodiments of the process of this invention and the apparatus associated therewith;

FIGURE 3 is a solubility diagram of CO_2 in liquid in various zones of a distillation column; and

FIGURE 4 is a C_2H_6 concentration diagram.

Detailed Description

In the process illustrated in FIGURE 1, a gaseous mixture 1 into column 2 there is introduced via conduit 1 a gaseous mixture having the following characteristics:

composition (by volume): 50% CO_2 , 45% CH_4 , 3% C_2H_6 , 2% C_3+ hydrocarbons;

pressure : about 36 bar;

temperature : about 300 K;

throughput rate : 100 mol/sec.

After being cooled to about 230 K in a heat exchanger 3, the gaseous mixture is introduced into column 2, operated under a pressure of about 35 bar, and is fractionated therein into a methane-rich, gaseous fraction 4, removed at the head of column 2, as well as into a liquid fraction 6 rich in carbon dioxide, withdrawn at the bottom of column 2. Fractions 4 and 6 are heated in heat exchangers 5 and 7 respectively to about 300 K.

The methane-rich fraction 4 contains at most 2% CO_2 ; the withdrawn quantity is about 43 mol/sec. The CO_2 -rich fraction 6 contains about 87% CO_2 , the withdrawn quantity is about 43 mol/sec. The pressure of the two fractions 4 and 6 is respectively about 34 bar.

The temperatures in column 2 range between about 180 K (head) and about 260 K (bottom). In the zone containing the head condenser 8, (approximately in the upper third of column 2) a portion of the CO₂ would 5 ordinarily be precipitated in solid form owing to the conditions present at that location.

In order to avoid such precipitation, a liquid stream 9 is withdrawn from column 2 approximately at the level of the middle of the column, the characteristics 10 of this stream being 42% CO₂, 21% C₂H₆, 37% CH₄, 25 mol/sec. This stream 9 is divided into two partial streams which are heated and vaporized in heat exchanger 10 and/or 15 heat exchanger 11 and are subsequently recombined. The stream 9 is then compressed in a compressor 12 to about 50 bar and, after removal of the heat of compression in a cooler 13, introduced at about 300 K into a membrane separation unit 14 provided with semipermeable membranes. Based on the differential permeabilities of the membranes for the various gaseous components, a fraction 15 with 20 about 73% CO₂ (14 mol/sec with about 1.5 bar) is removed on the low-pressure side of the separator 14, whereas a fraction 16 depleted in CO₂ (about 3% CO₂, 45% C₂H₆, 52% CH₄, 11 mol/sec) is obtained on the high pressure side of 25 the separator. The semipermeable membrane is e.g. cellulose acetate.

After the predominant part of the CO₂ has thus been separated, the remaining gas is cooled in heat exchanger 10, expanded, and thereby at least partially liquefied, and finally returned into column 2 below 30 (conduit 17) or above (dashed-line conduit 18) of the

head condenser 8. If desirable, the stream 16 can also be recycled in an entirely gaseous condition to the column. This could be advantageous with respect to the construction of the heat exchangers 10, 33 or 8 in as much as it might be advantageous to condense the recycled stream in the condenser of the column rather than in an external exchanger. This depends on a number of factors such as heat loads, enthalpy-temperature diagrams, gas-liquid velocities, construction limits etc. It might also be advantageous with respect to distribution of the recycled C_2H_6 within the column or cooling coils.

Furthermore, if desired, the CO_2 -rich fraction 15, after compression, can be mixed with the CO_2 -rich fraction 6 from column 2. In this way, a larger quantity of CO_2 can be passed, for example, to a tertiary oil recovery system and the gas recovered therefrom can after dehydration and other necessary preprocessing be treated as feed gas in conduit 1.

In the same apparatus operating in analogous manner, it is also possible to rectify a gaseous mixture which, during fractionation in column 2, would otherwise form a substantially azeotropic mixture. Examples of such a mixture include but are not limited to mixtures of CO_2 with C_2H_6 and other hydrocarbons, and H_2S with C_2H_6 and other hydrocarbons.

FIGURE 2 illustrates a system similar to that of FIGURE 1, but with the difference being that separation of CO_2 from the liquid stream 9 withdrawn from column 2 takes place by scrubbing rather than by membrane separation. (Corresponding structural components bear reference numerals identical to those in FIGURE 1.)

The liquid stream 9 taken from column 2 is heated and vaporized in heat exchanger 20 and subsequently compressed in compressor 12. As an alternative to compressor 12, it is also possible to provide a liquid pump upstream of heat exchanger 20.

In order to separate the CO_2 , the compressed gas is fed to a scrubbing column 21 where the CO_2 is absorbed by a chemical or physical scrubbing medium. Examples of a physical scrubbing agent include, but are not

limited to, N-methyl-2-pyrrolidone, and for a chemical scrubbing medium, methyldiethanolamine. The preferred scrubbing medium is methyldiethanolamine in water.

A gas extensively free of CO_2 is removed in conduit 32 from the head of the scrubbing column 21; after being cooled in cooler 33, this gas is expanded and reintroduced into column 2 either via conduit 34 below the head condenser 8 or via the conduit 35, illustrated in dashed lines, above the head condenser 8. Recycling takes place, depending upon requirements, in the gaseous or liquid condition. Depending on the scrubbing medium used and column temperatures, it may be necessary to remove traces of the scrubbing medium from the stream 32 before returning it to the column in order to prevent precipitation of solid phases in the heat exchanger 33, valves 34 or 35 or column 2. In the case of methyl-diethanolamine dissolved in water, a solid adsorbent may be used.

At the bottom of the scrubbing column 21, a liquid 22 is removed containing essentially CO_2 and the scrubbing medium. The liquid is heated in a heat exchanger 23, expanded, and fed to a phase separator 24 where a CO_2 -rich fraction 25 is withdrawn overhead. The liquid fraction 26 from phase separator 24 is expanded and introduced into a column 27 wherein extensive fractionation takes place into a gaseous overhead fraction rich in CO_2 withdrawn via conduit 28 and into a liquid fraction essentially containing regenerated scrubbing medium and withdrawn via conduit 29. The scrubbing medium in 29 is returned into scrubbing column 21 by means of a pump 30, but prior to recycling, cooling of the scrubbing medium is effected in a heat exchanger 31.

FIGURE 3 is a diagram of the solubility of CO_2 in the interior of column 2, the ordinate being the temperature plotted in Kelvin and the abscissa being the CO_2 proportion in the liquid, in percent. The curve 36 describes the solubility limit of CO_2 , below which CO_2 precipitates in the solid phase. Curves 37 and 38 indicate the CO_2 concentration in the liquid on the column plates, namely for the zone between the head of the column (A) and the point of introduction of the

feed stream 1 (B). The dashed-line curve 37 shows the course of distillation without removal, and curve 38 demonstrates the course with the removal of liquid at 9, and recycling of said liquid after separation of 5 a large part of the CO₂. It can be seen from this illustration that, without utilizing the present invention, CO₂ would be deposited in solid form between points C and D, by operating according to this invention, the CO₂ remains clearly above the solubility limit thereby avoiding 10 the deposition of solids.

FIGURE 4 is a graph of the concentration of C₂H₆ in column 2 having a total of 12 theoretical plates. The number, starting from the bottom of the column, 15 of the theoretical plates is plotted as the ordinate against the C₂H₆ concentration of the liquid in molar percent as the abscissa. The arrow 39 symbolically represents the withdrawal of liquid via conduit 9 on the 9th theoretical plate and return thereof via conduit 17 or 34 on the 12th theoretical plate, respectively. 20 Without such recirculation, the curve 40 in dashed lines represents the C₂H₆ concentration, whereas solid curve 41 is obtained using the recirculation mode of this invention. It can be seen that the liquid to be recycled is withdrawn at the point of highest ethane concentration, 25 and that the ethane concentration in the region of maximum concentration clearly increases by utilizing the process of this invention. Since CO₂ is highly soluble in liquid ethane, the increased ethane concentration is a further factor in preventing CO₂ precipitation.

Fig. 5 shows an example for the separation of a mixture containing an approximate azeotropic mixture. A mixture 42 of e.g. 40% C_2H_6 , 40% H_2S and 20% n C_4H_{10} is cooled in a cooler 43 and fed to a distillation column 44. In the column 44, H_2S and 5 C_2H_6 tend to form an azeotropic mixture, if the concentration of C_2H_6 is near 100%.

A liquid side stream 45 is withdrawn from below the middle of column 44, is pumped by a pump 46 through an evaporator 47 into a membrane separation unit 48. A fraction 54 enriched 10 in H_2S is removed on the low-pressure side of the separator 48, whereas a fraction 49 depleted in H_2S is obtained on the high pressure side of the membrane. This fraction containing a high concentration in C_4H_{10} is cooled and liquified in a cooler 50, expanded in valve 51, and recycled 15 into column 44 above the point of withdrawal. By this, the concentration of C_4H_{10} in the column will be increased with the result that the C_2H_6/H_2S - azeotrope in the upper part of the column can be broken. C_2H_6 is withdrawn via line 52 from the head of column 44, a liquid mixture of n C_4H_{10} with 20 H_2S is withdrawn from the sump of column 44 by line 53.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

I CLAIM:

1. A process for fractionating a gaseous mixture by distillation in a fractionating column wherein, during distillation, components of the gaseous mixture tend to form a substantially azeotropic mixture of an acid gas and hydrocarbon, or wherein at least one of the components of the gaseous mixture tends to freeze out in a nonhydrated form, said process comprising withdrawing a side stream fluid from the column during fractionation, and separating said side stream fluid so as to remove preferentially at least a portion of one of the components of the substantially azeotropic mixture or of the at least one of the components tending to freeze out, and recycling resultant depleted side stream to said fractionating column.

2. A process according to claim 1, wherein said side stream fluid is withdrawn, height-wise, from approximately the middle or upper third of the column.

3. A process according to claim 1, wherein said separating of said side stream is conducted by a physical or chemical scrubbing step.

4. A process according to claim 1, wherein said separating of said side stream is conducted by diffusion on semipermeable membranes.

5. A process according to claim 1, wherein the gaseous mixture to be fractionated comprises at least one of H_2S and CO_2 .

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6. A process according to claim 1, wherein the gaseous mixture contains an acid gas, as well as two other components having differing boiling points thereby providing an essentially three-component gas having components of low, intermediate and high boiling points, and wherein the side stream fluid is withdrawn from the column at a zone where the component having the intermediate boiling point has about the highest concentration.

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10 7. A process according to claim 1, wherein the depleted side stream is recycled into the column above the point of withdrawal.

8. A process according to claim 5, wherein the acid gas proportion of the depleted side stream fluid is at most 5%.

15 9. A process according to claim 5, wherein a stream enriched in acid gas is recovered as bottoms from said fractionating column, another stream enriched in acid gas is removed from said side stream fluid, and said two enriched streams are combined.

20 10. A process according to claim 1, wherein the gaseous mixture to be fractionated is a CO_2 -containing motive gas recycled from tertiary oil recovery, wherein a gas enriched in CO_2 is recovered from the bottom of said fractionating column and further comprising employing said CO_2 -enriched gas as motive gas in said tertiary oil recovery.

25 11. A process according to claim 10, wherein a stream enriched in CO_2 is recovered as bottoms from said fractionating column, another stream enriched in CO_2 is removed from said side stream fluid, and said two enriched streams are combined.

30 12. A process according to claim 5, wherein the gaseous mixture consists essentially of methane, ethane, CO_2 , the side stream fluid is separated so as to form a stream depleted in CO_2 but enriched in ethane and recycling the resultant depleted stream enriched in ethane, to the fractionating column.

13. A process according to claim 12, wherein said separating of said side fluid is conducted by diffusion on semipermeable membranes.

5 14. A process according to claim 13, wherein the depleted side stream is recycled into the column above the point of withdrawal.

10 15. A process according to claim 1, wherein components of the gaseous mixture tend to form a substantially azeotropic mixture and the depleted side stream is recycled into the column below the point of withdrawal.

15 16. A process for fractionating a gaseous mixture by distillation in a fractionating column wherein, during distillation, at least one of the components of the gaseous mixture tends to freeze out, said process comprising withdrawing a fluid from the column during fractionation, and separating said fluid so as to remove preferentially the at least one of the components tending to freeze out, and recycling resultant depleted stream to said fractionating column.

20 17. A process according to claim 16, wherein said separating of said fluid is conducted by diffusion on semipermeable membranes.

25 18. A process according to claim 16, wherein the gaseous mixture to be fractionated contains an acid gas and a hydrocarbon.

30 19. A process according to claim 16, wherein the gaseous mixture to be fractionated is a CO₂-containing motive gas recycled from tertiary oil recovery, wherein a gas enriched in CO₂ is recovered from the bottom of said fractionating column and further comprising employing said CO₂-enriched gas as motive gas in said tertiary oil recovery.

35 20. A process according to claim 16, wherein said separating of said fluid is conducted by diffusion on semipermeable membranes.

40 21. Apparatus for conducting the process of claim 1, comprising distillation column means, side stream conduits connected to the column for the withdrawal and return of a fluid, and membrane separation means in communication with the withdrawal conduit and the return conduit.

22. A process for fractionating a gaseous mixture by distillation in a fractionating column wherein, during distillation, at least one of the components of the gaseous mixture is present in the fractionating column in a sufficient concentration to freeze out in a non-hydrated form as a solid under distillation conditions in the column in the absence of a preventive step and another one of the components is present in the fractionating column in liquid phase, said another one of the components having the highest dissolving capacity for the freezable component, said process comprising withdrawing a sidestream liquid from the column during the fractionation at a point in the column where: (a) the freezable component is at a concentration lower than the maximum concentration and (b) where the high dissolving component is at substantially the maximum concentration, and separating said fluid so as to remove preferentially the at least one of the components and recycling resulted depleted stream to said fractionating column, said depleted stream having a higher dissolving capacity for the at least one of the components than the stream withdrawn.

23. A process according to claim 22, wherein said sidestream fluid is withdrawn, height-wise, from approximately the middle or upper third of the column.

24. A process according to claim 22, wherein said separating of said sidestream is conducted by a physical or chemical scrubbing step.

25. A process according to claim 22, wherein said separating of said side fluid is conducted by diffusion on semipermeable membranes.

26. A process according to claim 22, wherein the gaseous mixture to be fractionated contains an acid gas and a hydrocarbon.

27. A process according to claim 26, wherein the acid gas proportion of the depleted sidestream fluid is

at most 5 mol%.

28. A process according to claim 22, wherein a stream enriched in CO₂ is recovered as bottoms from said fractionating column, another stream enriched in CO₂ is removed from said sidestream fluid, and said two enriched streams are combined.

29. A process according to claim 28, wherein said separating of said fluid is conducted by diffusion on semipermeable membranes.

30. A process according to claim 22, wherein the gaseous mixture to be fractionated is a CO₂-containing motive gas recycled from tertiary oil recovery wherein a gas enriched in CO₂ is recovered from the bottom of said fractionating column and further comprising employing said CO₂-enriched gas as motive gas in said tertiary oil recovery.

31. A process according to claim 30, wherein said separating of said fluid is conducted by diffusion on semipermeable membranes.

32. A process according to claim 22, wherein said gaseous mixture to be fractionated consists essentially of methane, carbon dioxide and ethane, the latter being the component having the highest dissolving capacity for carbon dioxide.

33. A process according to claim 32, wherein the fluid withdrawn from the column during fractionation is separated to remove carbon dioxide and to obtain an ethane-enriched liquid, said liquid being recycled to the fractionating column.

34. A process according to claim 33, wherein the ethane-enriched fluid is recycled into the column above the point of withdrawal.

35. A process according to claim 34, wherein the withdrawn fluid is separated by semi-permeable membranes to remove both carbon dioxide and methane selectively from the fluid, thereby obtaining an enriched stream of

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ethane which is recycled into the column.

36. A process according to claim 22, wherein the component which is removed from the sidestream is also the main component which is gathered in the sump of the fractionating column.

37. A process according to claim 22, wherein the gaseous mixture contains CO₂, said CO₂ being the component which is removed from the sidestream.

38. A process according to claim 28, wherein the gaseous mixture to be fractionated is a gas recycled from tertiary oil recovery.

39. A process according to claim 34, wherein the gaseous mixture to be fractionated consists essentially by volume of about 5-20% methane, about 50-90% carbon dioxide and about 2-10% ethane.

40. A process for fractionating a gaseous mixture by distillation in a fractionating column wherein, during distillation, at least two components of the gaseous mixture are present in a sufficient concentration to form a substantially azeotropic mixture in the absence of a preventative step, said process comprising withdrawing a side stream fluid from the column during fractionation, and separating said side stream fluid so as to remove preferentially at least a portion of one of the components of the substantially azeotropic mixture and recycling resultant depleted side stream to said fractionating column at a point below the point of withdrawal of said side stream.

41. A process according to claim 40, wherein said side stream fluid is withdrawn, height-wise, from approximately the middle of the column.

42. A process according to claim 40, wherein said separating of said side stream is conducted by a physical or chemical scrubbing step.

43. A process according to claim 40, wherein said separating of said side fluid is conducted by diffusion

on semipermeable membranes.

44. A process according to claim 40, wherein the gaseous mixture to be fractionated contains an acid gas and a hydrocarbon.

45. A process according to claim 44, wherein the acid gas proportion of the depleted side stream fluid is at most 5%.

46. A process for fractionating a gaseous mixture by distillation in a fractionating column, said gaseous mixture consisting essentially of about 5-20% methane, about 50-90% carbon dioxide, and about 2-10% ethane, wherein, during distillation, CO₂ is present in the fractionating column in a sufficient concentration to freeze out as a solid under distillation conditions in the column in the absence of a preventive step, said process comprising fractionating the mixture to obtain methane-enriched overhead and a CO₂ enriched bottoms fraction, withdrawing a sidestream liquid from the column during fractionation, said sidestream liquid being withdrawn at a point where ethane is enriched in the liquid and where CO₂ is present in a lower concentration than in the bottoms fraction, and separating said sidestream liquid so as to remove preferentially the CO₂ and recycling resultant CO₂-depleted stream further enriched in ethane to said fractionating column, said depleted stream having a higher dissolving capacity for CO₂ than the stream withdrawn.

47. A process according to claim 46, wherein said separating of said sidestream is conducted by diffusion on semipermeable membranes.

48. A process according to claim 46, wherein the gaseous mixture to be fractionated is a CO₂-containing motive gas recycled from tertiary oil recovery, and the gas enriched in CO₂ recovered from the bottom of said fractionating column is employed as motive gas in said

tertiary oil recovery.

49. A process according to claim 48, wherein said separating of said sidestream is conducted by diffusion on semipermeable membranes.

50. A process according to claim 46, wherein the enriched ethane stream is recycled into the column above the point of withdrawal.

52. A process according to claim 51, wherein the withdrawn sidestream is separated by semi-permeable membranes to remove both carbon dioxide and methane selectively from the sidestream, thereby obtaining an enriched stream of ethane which is recycled into the column.

53. A process according to claim 46, wherein the sidestream is withdrawn from the column at the zone of the highest ethane concentration therein.

54. A process according to claim 53, wherein the enriched ethane stream is recycled into the column above the point of withdrawal.

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"PROCESS AND APPARATUS FOR FRACTIONATION
OF A GASEOUS MIXTURE"

Abstract

In fractionating a gaseous mixture an acid gas and e.g. hydrocarbon in a column wherein, during distillation, components of the gaseous mixture tend

- 5 to form a substantially azeotropic mixture, or at least one of the components of the gaseous mixture tends to freeze out, withdrawing a side stream fluid from the column during fractionation, and separating said side stream fluid, e.g. by membranes or scrubbing, so as
- 10 to remove preferentially at least a portion of one of the components of the substantially azeotropic mixture, or of the at least one of the components tending to freeze out, and recycling resultant depleted side stream to said fractionating column.

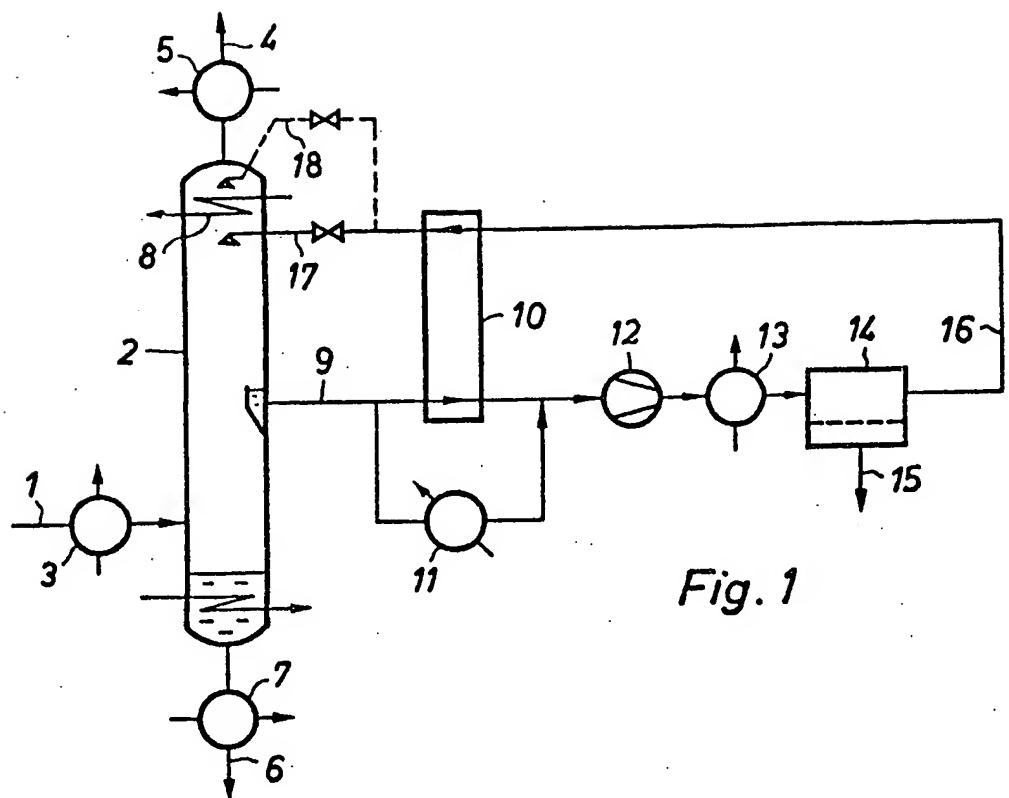


Fig. 1

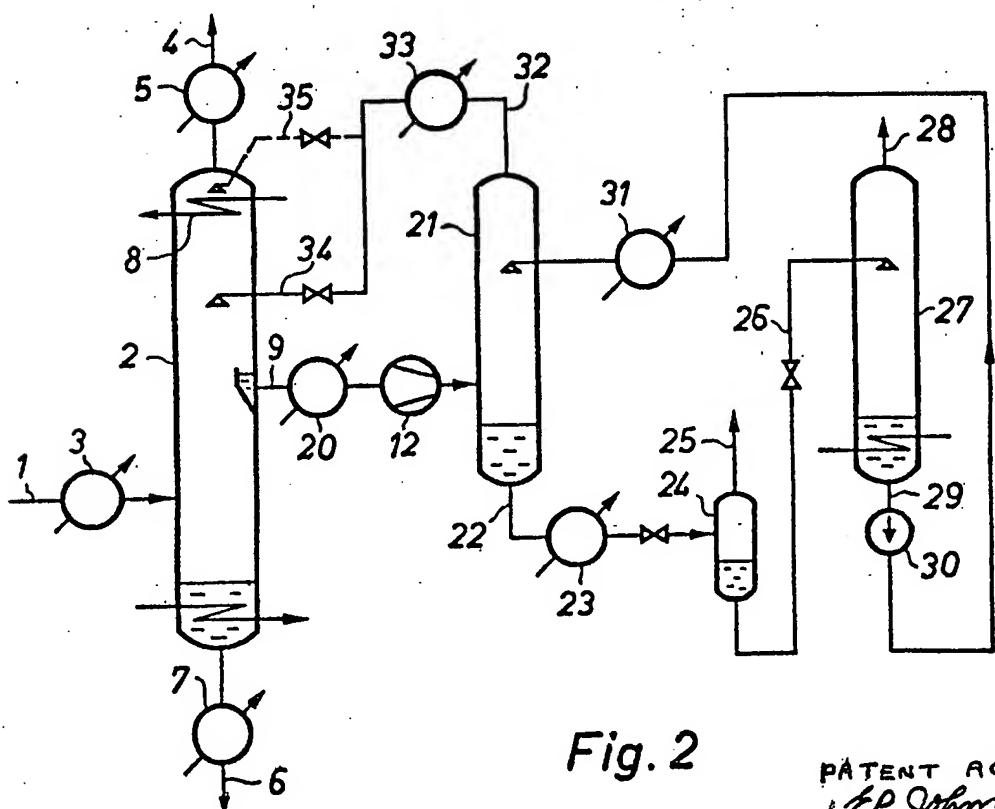


Fig. 2

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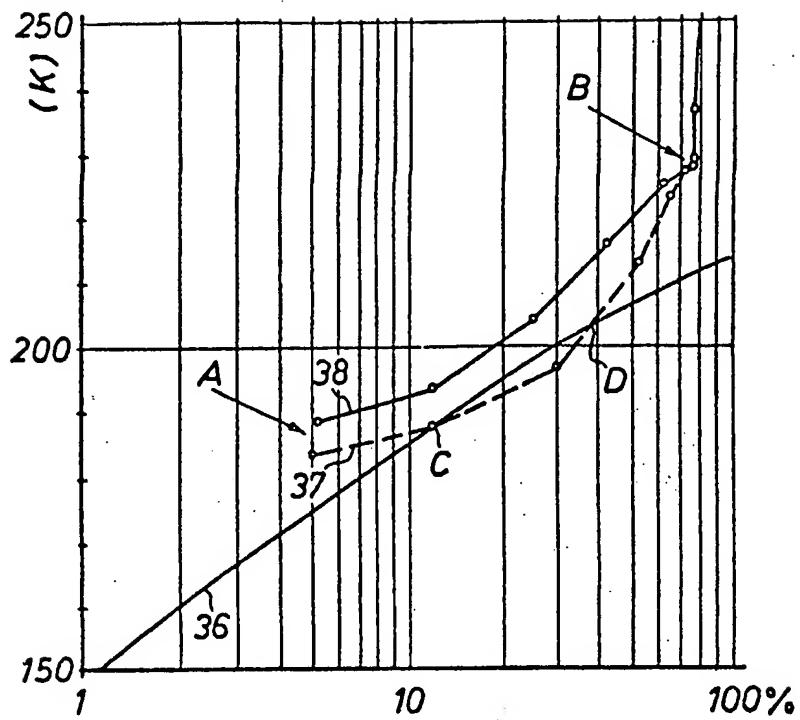


Fig. 3

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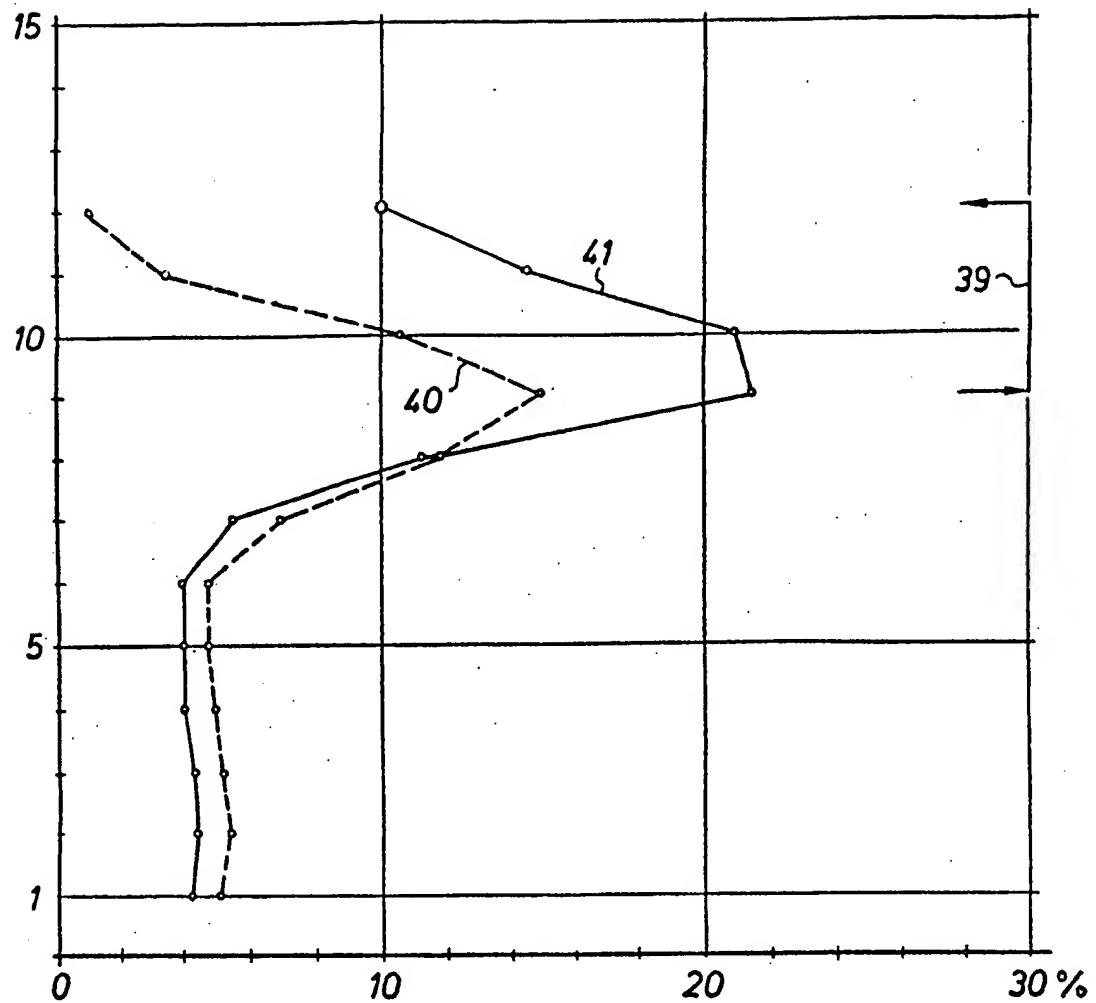


Fig.4

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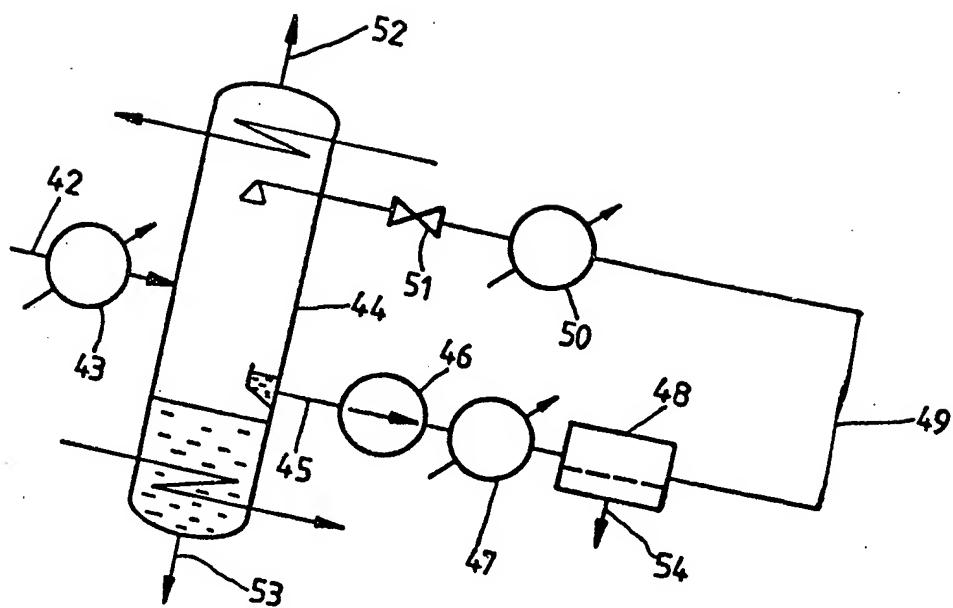


Fig. 5